

# PATENT SPECIFICATION

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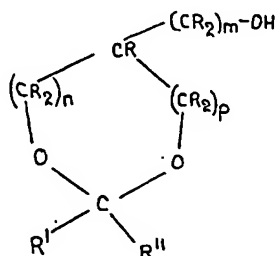
## (54) PLASTICISED POLYAMIDES

(71) We, CHEMISCHE WERKE HÜLS AKTIENGESELLSCHAFT, a German Company, of 4370 Marl, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Compounds which contain hydroxyl, ester or amide groups (Hopff—Müller—Wenger, Die Polyamide (1954), pages 188 ff), or sulphonamides (Kunststoff Handbuch, Polyamide (1966), page 238 f), are mainly used for plasticising polyamides.

The known plasticisers however cannot be added in large concentrations, for example in amounts up to 40%, by weight referred to the polyamide, since the moulding material thus thus produced is difficult to process. The best known plasticisers are exuded from the injection mouldings or extruded mouldings.

We have now found that these disadvantages can be prevented if cycloacetal alcohols or cycloketalalcohols having the general formula



in which  $n = 1$  or  $2$ ,  $p = 0$  or  $1$ ,  $m = 0$  to  $14$  and  $p + m$  is greater than or equal to  $1$ ,  $R$ ,  $R'$  and  $R''$  denote a univalent organic radical which may if desired be substituted,  $R''$  having at least three carbon atoms and  $R$  and  $R'$  also denoting hydrogen atoms and  $R'$  and  $R''$  may also together form a ring, which have a boiling point of at least  $250^\circ\text{C}$ , can be used as plasticisers for polyamides.

In particular, the substituents  $R$ ,  $R'$  and  $R''$  have the following meaning:

[Price 25p]

$R$  is in most cases a hydrogen atom or an alkyl radical having 1 to 5 carbon atoms,

$R'$  is a hydrogen atom, an aromatic radical or an alkyl radical having 1 to 8 carbon atoms,

$R''$  is an aromatic radical or an alkyl radical having 3 to 10 carbon atoms.

$R'$  and  $R''$  may together form a bivalent organic radical having 4 to 11 carbon atoms, so that the compound which is thus formed is a spiro compound.

Polyamides are understood in this context to be homopolycondensates of aliphatic, cycloaliphatic or aromatic dicarboxylic acids and diamines, as for example the polycondensation products of adipic acid, sebacic acid or terephthalic acid and hexamethylenediamine, phenylene diamine, as well as polycondensation products of amino carboxylic acids as for example  $\omega$ -aminoundecane acid, or polymerisation products of lactams as for example caprolactam or laurolactam, and also copolymers or mixed polycondensates from diamines and dicarboxylic acids and/or aminocarboxylic acids and/or lactams.

The cycloacetal alcohols and cycloacetal alcohols (for the production of which no protection is claimed within the scope of this application) may be obtained in a known manner (see Houben-Weyl, Methoden der organischen Chemie, Sauerstoffverbindungen, I — Teil 3 (1965), p213) by reacting a triol with an aldehyde or a ketone.

Suitable triols on which the cycloacetal alcohols or cyclo ketal alcohols are based are for example glycerol, hexanetriol-1,2,6, hexanetriol-1,3,6 and 1,1,1-trimethylol propane.

Aldehyde components which may be used in the cycloacetal alcohols are for example: n-butyraldehyde, isobutyraldehyde, 2-ethylcaproaldehyde, benzaldehyde, m-tolualdehyde, p-tolualdehyde, o-chlorobenzaldehyde, p-chlorobenzaldehyde, salicylaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, o-methoxybenzaldehyde and anisaldehyde.

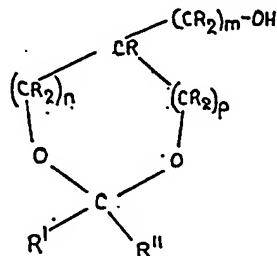
Suitable ketone components in the cycloacetal alcohols are for example: pentanone-(2), hexanone-(2), hexanone-(3), methyl-t-butyl-

	ketone, diisopropylketone, diisobutylketone, undecanone-(6), acetophenone, benzophenone, mesityl oxide, cyclopentanone, cyclohexanone, cyclododecanone.	
5	Compounds which are particularly suitable as plasticisers are the following:	
	2,2 - pentamethylene - 4 - hydroxymethyl-dioxolane - (1,3)	
10	2 - isopropyl - 4 - hydroxymethyldioxolane - (1,3)	
	2 - n - heptyl - (3') - 4 - hydroxymethyl-dioxolane - (1,3)	
	2 - methyl - 2 - phenyl - 4 - hydroxymethyl-dioxolane - (1,3)	
15	2 - phenyl - 4 - hydroxymethyldioxolane - (1,3)	
	2,2 - diphenyl - 4 - hydroxymethyldioxolane - (1,3)	
	2,2 - undecamethylene - 4 - hydroxymethyl-dioxolane - (1,3)	
20	2,2 - diisopropyl - 4 - hydroxymethyl-dioxolane - (1,3)	
	2,2 - pentamethylene - 4 - (4' - hydroxy - n - butyl) - dioxolane - (1,3)	
25	2 - isopropyl - 4 - (4' - hydroxy - n - butyl) - dioxolane(1,3)	
	2 - n - heptyl - (3') - 4 - (4'' - hydroxy - n - butyl) - dioxolane(1,3)	
	2 - methyl - 2 - phenyl - 4 - (4' - hydroxy - n - butyl) - dioxolane(1,3)	
30	2 - phenyl - 4 - (4'hydroxy - n - butyl) - dioxolane(1,3)	
	2,2 - diphenyl - 4 - (4'hydroxy - n - butyl) - dioxolane(1,3)	
35	2,2 - undecamethylene - 4 - (4' - hydroxy - n - butyl) - dioxolane(1,3)	
	2,2 - diisopropyl - 4 - (4' - hydroxy - n - butyl) - dioxolane(1,3)	
	2,2 - pentamethylene - 4 - (3' - hydroxypropyl) - dioxan(1,3)	
40	2 - isopropyl - 4 - (3' - hydroxypropyl) - dioxan(1,3)	
	2 - n - heptyl - (3') - 4 - (3'' - hydroxypropyl) - dioxan(1,3)	
45	2 - methyl - 2 - phenyl - 4 - (3' - hydroxypropyl) - dioxan(1,3)	
	2 - phenyl - 4 - (3' - hydroxypropyl) - dioxan(1,3)	
	2,2 - diphenyl - 4 - (3' - hydroxypropyl) - dioxan(1,3)	
50	2,2 - undecamethylene - 4 - (3' - hydroxypropyl)dioxan(1,3)	
	2,2 - diisopropyl - 4 - (3' - hydroxypropyl)-dioxan(1,3)	
55	2,2 - pentamethylene - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	
	2 - isopropyl - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	
	2 - n - heptyl - (3') - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	
60	2 - methyl - 2 - phenyl - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	
	2 - phenyl - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	
	2,2 - diphenyl - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	65
	2,2 - undecamethylene - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	
	2,2 - diisopropyl - 5 - ethyl - 5 - hydroxymethyl - dioxan(1,3)	70
	They are used as primary plasticisers.	
	The plasticisers are added to the homopolyamide or copolyamide in the hitherto conventional manner. For this purpose the polyamide granules or powder are mixed with the desired amount of cycloacetal alcohol or cycloketol alcohol below the softening point of the polyamide in a suitable mixer, and are then immediately processed above the softening temperature of the polyamide into finished parts or semi-finished parts in a processing machine adapted for this purpose, or are extruded in a suitable extruder above the softening temperature of the polyamide, after mixing, and granulated again. The cycloacetal alcohols or cycloketol alcohols may also be metered into the melt in the extruder.	
	The cycloacetal alcohols or cycloketol alcohols can also be added to a polyamide solution on account of their good compatibility with almost all organic solvents. This solution is then processed by means of suitable processing machines and the solvent is removed from the finished article in the usual manner.	
	In the case of homopolyamides the cycloacetal alcohols or cycloketol alcohols are generally used in amounts of 5 to 40% by weight based on the weight of the homopolyamide, and in the case of copolyamides in amounts of 5 to 30% by weight based on the weight of the copolyamide.	
	If desired, the cycloacetal alcohols or cycloketol alcohols may also be used in admixture with known plasticisers in all proportions.	
	Plasticised polyamides which contain cycloacetal alcohols or cycloketol alcohols as plasticiser have a particularly good thermal stability under load and toughness under cold conditions. In particular, these products have the advantage that they can be used even in high concentrations and the polymers thus plasticised can be thermoplastically processed. Polyamides produced using the hitherto known plasticisers cannot be processed by extrusion and injection moulding if they have a high amount of plasticiser.	
	The result obtained using the cycloacetal alcohols or cycloketol alcohols in accordance with the invention are collected together in the following table, and compared with known plasticisers.	
	<b>EXAMPLE</b>	
	In each case 10 kg of polylaurolactam in granule form and 2.5 kg of the plasticiser employed are homogenised in a slowly running mixer and continuously fed to a double screw extruder. The mixture is plasticised and granulated at 200 to 250°C.	

	DIN-standard	2,2-Pentamethylene-4-hydroxymethyl-1,3-dioxolane	2-Iso-propyl-4-hydroxymethyl-1,3-dioxolane	2-Methyl-2-phenyl-4-hydroxymethyl-1,3-dioxolane	2,2-Pentamethylene-5-hydroxymethyl-1,3-dioxolane	2-Methyl-5-ethyl-2-phenyl-5-hydroxymethyl-1,3-dioxolane	Comparison Examples		
							Benzol-sulfon-N-methyl-amid	Toluol-sulfon-säure-amid	Tolylaurin-lactam ohne Weich-
limiting bending strain [kp/cm <sup>2</sup> ]	53 452	230	220	230	230	240	230	250	800
yield stress [kp/cm <sup>2</sup> ]	53 455	220	230	210	210	220	220	230	530
extension under yield stress [%]	53 455	30	30	30	30	30	25	30	15
ball-pressure hardness after 10 secs. [kp/cm <sup>2</sup> ]	53 456	350	360	350	360	370	350	350	1000
notch impact strength [cmkp/cm <sup>2</sup> ]	53 453	no bending 20	no bending	no bending 80% no bending 6,3	no bending 17	no bending 10	no bending 12	no bending 12	11 9
at 20°C ± 0°C -20°C -40°C		5,9 3,2	4,3 3,1	2,5 2,5	2,5	2,6	4,5 2,0	3,0 2,3	8 7
1 mm bending of a small standard test bar under 18.5 kp/cm <sup>2</sup>	—	109	—	115	108	105	108	109	—
plasticiser exudate in injected moulded parts		none	none	none	none	none	strong	slight	—

## WHAT WE CLAIM IS:—

1. A process for plasticising a polyamide which comprises mixing the polyamide with a plasticiser comprising a cycloacetal alcohol or cycloketal alcohol of the general formula:



in which  $n = 1$  or  $2$ ,  $p = 0$  or  $1$ ,  $m = 0$  to  $14$  and  $p + m \geq 1$ ,  $R$ ,  $R'$  and  $R''$  each independently denote a monovalent organic radical which may be substituted, wherein  $R''$  contains at least three carbon atoms,  $R$  and  $R'$  may also be hydrogen atoms and  $R'$  and  $R''$  may also together form a ring, having a boiling point of at least  $250^\circ\text{C}$ .

2. A process as claimed in claim 1 in which any organic radicals denoted by  $R$ ,  $R'$  or  $R''$  or by  $R'$  and  $R''$  together are hydrocarbon radicals.

3. A process as claimed in claim 1 or 2 wherein each  $R$  independently denotes a hydrogen atom or an alkyl radical having 1 to 5 carbon atoms.

4. A process as claimed in claim 1, 2 or 3 wherein  $R'$  denotes hydrogen or an alkyl radical having 1 to 8 carbon atoms.

5. A process as claimed in claim 1, 2 or 3 wherein  $R'$  denotes an aromatic radical.

6. A process as claimed in claim 1, 2, 3, 4 or 5 wherein  $R''$  denotes an aromatic radical.

7. A process as claimed in claim 1, 2, 3, 4

or 5 wherein  $R''$  denotes an alkyl radical having 3 to 10 carbon atoms.

8. A process as claimed in claim 1, 2 or 3 wherein  $R'$  and  $R''$  together denote a divalent radical having 4 to 11 carbon atoms, which together with the carbon atom to which it is attached, forms a ring.

9. A process as claimed in claim 3 in which the plasticiser is derived notionally or actually from the condensation of an aldehyde or ketone listed herein with a triol.

10. A process as claimed in claim 2 or 9 in which the plasticiser contains not more than 19 carbon atoms.

11. A process as claimed in claim 2, 9 or 10 in any of claims 3 to 8 as appendant to claim 2, in which all the  $R$ s in the radical denoted by  $(CR_2)_m$  denote hydrogen, and the other  $R$ s each independently denote hydrogen or an alkyl radical of 1 to 5 carbon atoms.

12. A process according to any of claims 1 to 11, wherein a cycloacetal alcohol or cycloketal alcohol is added to a polyamide in an amount of 5 to 40% by weight.

13. A process according to any of claims 1 to 12, wherein a known plasticiser is mixed with the cycloacetal alcohol or cycloketal alcohol.

14. A process for plasticising polyamides substantially as hereinbefore described.

15. A composition comprising a known plasticiser for polyamides, and a plasticiser as specified in any of claims 1 to 11.

16. A plasticised polyamide when prepared by a process as claimed in any of claims 1 to 14.

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